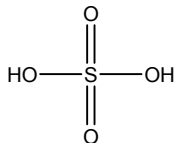


STRONG INORGANIC ACID MISTS CONTAINING SULFURIC ACID

CAS No. 7664-93-9 (Sulfuric Acid)

First listed in the *Ninth Report on Carcinogens*



CARCINOGENICITY

Occupational exposure to strong inorganic acid mists containing sulfuric acid is *known to be a human carcinogen*, based on sufficient evidence of carcinogenicity from studies in humans that indicate a causal relationship between exposure to strong inorganic acid mists containing sulfuric acid and human cancer (reviewed in IARC V.54, 1992).

Occupational exposures to strong inorganic acid mists containing sulfuric acid are specifically associated with laryngeal and lung cancer in humans. Steenland et al. (1988) reported on studies of one U.S. cohort of male workers in pickling operations in the steel industry, which showed excesses of laryngeal cancer after adjusting for smoking and other potential confounding variables [standardized incidence rate ratio (SIR) for laryngeal cancer was 2.30 (95% confidence interval [CI], 1.05-4.36)]. In a ten-year follow-up, Steenland (1997) reported a laryngeal cancer rate ratio of 2.2 (95% CI, 1.2-3.7), consistent with previous findings from this cohort. In a nested case-control study of workers in a U.S. petrochemical plant, Soskolne et al. (1984) found a dose-response for laryngeal cancer risk among workers exposed to moderate (odds ratio [OR] of 4.6; 95% CI, 0.83-25.35) or high levels (OR of 13.4; 95% CI, 2.08-85.99) of sulfuric acid. In a Canadian population based case-control study, after controlling for tobacco and alcohol use and including only the most specific exposure scale, Soskolne et al. (1992) also observed a dose-response for laryngeal cancer risk in workers exposed to sulfuric acid mist, with ORs of 2.52 (95% CI, 0.80-7.91) at the lowest level of exposure and 6.87 (95% CI, 1.00-47.06) at the highest. A report of a similar population based case-control study in Canada by Siemiatycki (1991) suggested an increase in risk for oat-cell carcinoma of the lung (rate ratio [RR] of 2.0; 90% CI, 1.3-2.9). Steenland and Beaumont (1989), reporting on the same U.S. cohort of male workers in pickling operations described by Steenland et al. (1988), found an excess of lung cancer in these workers after adjusting for smoking and other potential confounding variables [standardized mortality ratio (SMR) for lung cancer was 1.36 (95% CI, 0.97-1.84)].

No adequate experimental animal carcinogenicity studies of sulfuric acid or strong inorganic acid mists containing sulfuric acid have been reported in the literature.

ADDITIONAL INFORMATION RELEVANT TO CARCINOGENESIS OR POSSIBLE MECHANISMS OF CARCINOGENESIS

The manufacture of isopropyl alcohol by the strong acid process, which uses sulfuric acid, has been identified by IARC as known to cause an increased incidence of cancer of the paranasal sinuses in workers (reviewed in IARC V.15, 1977).

The carcinogenic activity of sulfuric acid is most likely related to the genotoxicity of low pH environments. Reduced pH environments are known to enhance the depurination rate of DNA and the deamination rate of cytidine (IARC V.54, 1992).

PROPERTIES

Commercial sulfuric acid contains 93 to 98% H_2SO_4 and the rest water. Fuming sulfuric acid or oleum contains up to 80% free sulfur trioxide (SO_3). Sulfuric acid is very corrosive and desiccates organic matter on contact. Sulfuric acid emits SO_x upon thermal decomposition at 340 °C (Spectrum, 1996; Budavari, 1996).

Liquid sulfuric acid may exist in air as vapor or mist, most often as mist because of sulfuric acid's low volatility and its tendency to react with water. A mist has been defined by Hinds (1985; cited by IARC V.54, 1992) as a liquid aerosol formed by condensation of a vapor or atomization of a liquid.

Sulfuric acid mist has been the most extensively studied of the acid mists. Its human effects depend on many factors such as particle size, water solubility, free hydrogen ion concentration, and presence of other chemicals in the aerosol particle. Acid aerosols as a group have been designated one of six criteria pollutants by the U.S. Environmental Protection Agency because of their increasing presence from various human activities and their potential to cause or aggravate health effects, particularly within the respiratory tract. Sulfuric acid mist may contain aerosol particles up to a few micrometers in diameter; generally, the smaller the particle, the deeper it may penetrate into the lung. Local corrosive effects on skin and mucous epithelia from sulfuric acid mist may occur upon exposure to adequate levels (IARC V.54, 1992).

In some contexts in the literature reviewed, "acid strength" may be related to the concentration of H_2SO_4 in the solution. [The concentrations of H_2SO_4 range from 35.67% to 98.99% in industrial applications described in the IARC V.54 monograph as of concern for the generation of strong inorganic acid mists. Additional industries use oleum, concentrated sulfuric acid with free SO_3 concentrations up to 65%. For example, oleum with 40% free SO_3 is used in industrial nitrations and sulfonations (IARC V.54, 1992).] All of these concentrations would give aerosols considered to be strong inorganic acid mists containing sulfuric acid.

USE

Sulfuric acid is a widely used industrial chemical. Manufacture of fertilizers (both phosphate and ammonium sulfate) is the principal use of sulfuric acid. It is used as a reagent in many processes and usually appears in the end products as sulfate waste or spent acid (IARC V.54, 1992).

PRODUCTION

Sulfuric acid is the largest volume chemical produced in the United States (Kirschner, 1996). In 1996, the total production volume was 47,677 million tons (43,252 million metric tons [Mg]) (Chem. Eng. News, 1997). As of January 1996, there were 61 companies listed as producers of sulfuric acid (SRIa, 1996), 10 of which produced more than 1.0 million Mg each. The total annual capacity was listed as 48.36 million Mg of sulfuric acid in 1995. The five largest producers listed were IMC-Agrico Co., PCS Phosphate Co., Rhone-Poulenc, Inc., Cargill

Fertilizer, Inc., and Magma Metals with the following annual capacities: 8.88 million Mg, 6.286 million Mg, 2.937 million Mg, 2.766 million Mg, and 1.90 million Mg, respectively.

Sulfuric acid is used or produced during various manufacturing processes, during which sulfuric acid mists may be generated. In pickling, for instance, mist may escape from acid tanks when hydrogen bubbles and steam rise from the surface of the solution. Mist may be generated during a process when factors such as evaporative surface area, solution strength, temperature, and pressure combine to affect release or condensation of gases. Concentrations to which workers are exposed depend on proximity to the source and controls of ventilation and containment (IARC V.54, 1992).

EXPOSURE

Sulfuric acid is found naturally in volcanic locations, especially in volcanic gases (HSDB, 1997). According to the Toxic Chemical Release Inventory for 1995 (TRI95, 1997), the total reported anthropogenic environmental release of sulfuric acid was 26,486,002 lb (13,243 tons; 12,014 Mg).

Ambient air may contain particulate-associated mixtures of sulfuric acid and ammonium sulfates (sulfuric acid partially or completely neutralized by atmospheric ammonia). The relative amounts of sulfuric acid and total sulfates depend on meteorological and chemical parameters. Diammonium sulfate is usually the predominant atmospheric chemical species in the submicrometer particles. The presence of sulfuric acid and sulfates in the atmosphere is believed to be due to oxidation of sulfur dioxide in cloud water and other atmospheric media. The presence of ammonia may be due to anthropogenic pollution such as coke plant emissions. Ambient air concentrations of ammonium sulfates are very low in areas where anthropogenic sulfur dioxide emissions are low or far removed. Sulfuric acid and sulfate aerosol events (periods of distinct acidity) may be due to regional scale atmospheric stagnation episodes or to local sources of sulfur dioxide emissions (Johnson and Kumar, 1988; Burton et al., 1992; Schlesinger and Chen, 1994; Spengler et al., 1996). Ambient air concentrations of sulfuric acid are an order of magnitude or more lower than concentrations in occupational settings (IARC V.54, 1992).

The Toxic Chemical Release Inventory for 1995 (TRI95, 1997) includes a total of 1570 facilities reporting environmental releases of sulfuric acid. Among the 835 facilities reporting atmospheric sulfuric acid emissions, 221 facilities reported emissions of up to 200 lb/rep. (reported) yr. The remaining 614 facilities had emissions ranging from 200 lb to 7 million lb/rep. yr. The industries reporting releases were pulp and paper mills (SIC 2611 and 2621), petroleum refining (SIC 2911), phosphate fertilizers (SIC 2874), plastics products, not elsewhere classified (SIC 3089), industrial organic chemicals, not elsewhere classified (SIC 2869), and primary copper industries (SIC 3331).

Industrial processes in which occupational exposure to sulfuric acid mist has been examined include manufacture of isopropyl alcohol, lead batteries, nitric acid, phosphate fertilizers, soap and detergents, synthetic ethanol, sulfuric acid and pickling and other acid treatments of metals (IARC V.54, 1992).

IARC (V.54, 1992) also compiled the means and ranges of strong inorganic acid mist work area and personal air concentration measurements of up to $>1 \text{ mg/m}^3$ in pickling and other acid cleaning of metals and electroplating operations (measurements in 1977-1981).

The National Institute of Occupational Health and Safety (NIOSH, 1990) listed results of the National Occupational Exposure Survey (1981-1983), which reported 54,519 plants with potential workplace exposure to sulfuric acid. A total of 775,584 employees, including 173,650 female employees, were potentially exposed to sulfuric acid in the workplace.

REGULATIONS

EPA regulates sulfuric acid atmospheric emissions under the Clean Air Act regulations concerning Standards of Performance for New Stationary Sources and State Implementation Plans to prevent significant deterioration of air quality; CERCLA (Comprehensive Emergency Response, Compensation, and Liability Act) and EPCRA (Emergency Planning and Community Right-to-Know Act). The specific regulations are described in the Regulations table. EPA regulations pertaining primarily to sulfuric acid in effluents to water, to pesticide residues, or to solid wastes are not included. FDA regulations on sulfuric acid are not included since they relate to possible ingestion. NIOSHa (1974) recommended a ≤ 10 -hour time-weighted average (TWA) exposure of 1 mg/m^3 . The OSHA permissible exposure limit (PEL) for sulfuric acid in workroom air, the construction industry, and shipyards is 1 mg/m^3 as an 8-hour TWA. ACGIH (1996) also recommended a workroom air threshold exposure limit for sulfuric acid in strong inorganic mists (considered to be a suspected human carcinogen) of 1 mg/m^3 as an 8-hour TWA for a 40-hour work week. In addition, ACGIH recommended a short-term exposure limit (STEL) of 3 mg/m^3 . "Worker exposure by all routes should be controlled as low as possible below the TLV." Regulations are summarized in Volume II, Table A-37.